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Multifunctional cholesterol-based peroxide for modification of amino-terminated surfaces: Synthesis, structure and characterization of grafted layer

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ABSTRACT

A multifunctional cholesterol-based peroxide modifier – monoperoxided monocholesteryl pyromellitate (PChP) with residual acid chloride groups has been synthesized. The structure of the peroxide modifier was confirmed using IR and ^{1}H NMR spectroscopies. Grafted PChP coating was successfully fabricated onto amino-terminated glass surfaces. Thickness and refractive index of the coated layer, its morphology, wettability, and alignment of elongated PChP molecules, attached to the surface at different grafting times were characterized by means of ellipsometry, AFM, measurements of wetting contact angle and testing alignment of a nematic liquid crystal on the coatings. In a flat cell assembled of a pair of glass substrates coated with the PChP layer nematic molecules align preferentially tilted with respect to the cell normal, though in some place one finds homeotropic alignment, where nematic molecules are perpendicular to the surface. Liquid crystal textures visualize inhomogeneities in surface profile of the coated layer. Homeotropic alignment is observed in places where roughness of the layer is completely randomized in agreement with AFM data, providing visualization of evolution of the surface profile. Concentration of grafted molecules per area of the surface deduced from ellipsometry data suggests that PChP molecules are grafted to the surface rather densely already in about ten minutes.

1. Introduction

Modification of inorganic and polymer surfaces for formation of certain surface properties is one of the main trends in modern chemistry [1,2]. During recent years, some inorganic materials with hydroxyl groups, especially glass slides were widely used as an object for modification accounting for their cheapness and abundance [3,4]. Most frequently used substances for glass surface modification are silane coupling agents, including two types of functionality. First type is hydrolyzable groups, which can condense with other silanol groups. Second type of groups is non-hydrolyzable organic radicals that may possess a functionality that imparts desired characteristics. Using of some silanes, such as (3-aminopropyl)-triethoxysilane (APTES), for modification of glass surfaces has been widely described and is attractive for further immobilization of biomolecules, polymers or molecules with liquid crystal ordering [5–8]. Some researchers propose to use amino-covered glass slides with organosilanes for DNA immobilization [9]. Moreover, different metal oxide surfaces, such as SiO_2, TiO_2, ZrO_2, and SnO_2 have been amino-functionalized and can be used for future modifications and applications [10]. Therefore, modification of the amino-covered surfaces has essential interest for preparation of surfaces with new desirable properties.

In our opinion, multifunctional modifiers deserve special attention among diversities of the potential modifiers of the amino-covered surfaces. Multifunctional surface modifiers are agents that have three or more functional activities, with their main functionality being the ability to form a durable bond with intact or modified surfaces [11–13]. In addition, multifunctional surface modifiers attract increasing interest as precursors for fabrication of grafted Y-shape molecules [11].

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In our previous papers [14,15], the method of fabrication of polymer coatings using multifunctional oligoperoxide, grafted to a native glass surface functionalized with APTES, was reported. Inspired by strong progress on synthesis of new surface modifiers [11–13,16,17], we have developed and report in this paper a synthetic approach to a new multifunctional cholesterol-based peroxide modifier - monoperoxided monocholesteryl pyromellitate with residual acid chloride groups. The structure of the peroxide modifier was confirmed using IR and ^{1}H NMR spectroscopies. Grafted PChP coating was successfully fabricated onto amino-terminated glass surfaces. Ellipsometry, atomic force microscopy (AFM) and wetting contact angle measurements were used to analyze respectively the thickness, morphology and wettability of this novel coating.

To examine homogeneity of the modified surface as well as to get information on alignment of elongated molecular PChP fragments with respect to the surface, we inspect the coatings as alignment layers for a nematic liquid crystal. This characterization technique is based on high sensitivity of liquid crystal (LC) alignment to chemical nature and geometrical profile of the surface. Due to orientational elasticity the alignment of LC molecules, set by the surface, propagates through the bulk of a LC sample and in this regard there are at least two important aspects. On one hand, sensitivity of the LC alignment to the state of interface allows one for visualization of surface profile features. As a rule inhomogeneities of the surface and imperfections of its geometrical profile are reflected in the distribution of the LC director along the surface and thereby being visualized in a form of specific polarization microscopy textures allowing one for determination of the alignment of LC molecules at the surface. Uniform alignment indicates homogeneity of the surface. Presence of defects, which are often accompanied by amazingly beautiful colorful textures around them, visualizes surface inhomogeneities. On the other hand, alignment of the LC director at the surface dictates its orientation in the bulk. This property is used for preparation of LC cells with desired orientation of the director and finds its application in the LC display industry. New alignment layers for liquid crystals are in great demand. Alignment layers providing high pretilt angle for the nematic director are rare and are of special interest. Our results suggest that the PChP layer is a promising material for development of such an alignment layer.

Employing initiating polymerization from peroxide fragments, the grafted molecules can be transformed in Y-shape molecules. In addition, presence of cholesterol fragments in the structure of the modifier suggests this coating as being potentially biocompatible.

2. Experimental procedures

2.1. Synthesis of pyromellitic acid chloride

In a 500 ml round-bottomed flask equipped with a thermometer and a reflux condenser, connected with water scrubber, 43.6 g (0.2 mol) of pyromellitic dianhydride and 91.6 g (0.44 mol) of PCl_5 were mixed and boiled in the oil bath until the mixture became homogeneous. Afterwards, it was additionally mixed for 15–16 h at 130–135 °C**.** The reflux condenser was then replaced by a Liebig condenser and approximately 60–63 g of $POCl_3$ was distilled off during 8 h. Then the temperature of the mixture was increased to 180–185 °C. The crude product was recrystallized then from gasoline yielding 51.2 g (78.1%) of a colorless crystalline substance with the melting point at 67 °C (in accord with the literature value of 68 °C [18]) and acid number AN = 1373 mg KOH/g (calculated value 1368 mg KOH/g).

2.2. Synthesis of PChP with residual acid chloride groups

4.7 g (0,0143 mol) of pyromellitic acid chloride was dissolved in 10 ml of anhydrous dichlorethane. The solution was cooled down to 5 °C, and then 1.3 g (0.0143 mol) of tert-butylhydroperoxide and 1.13 g (0.0143 mol) of pyridine, dissolved in 10 ml of anhydrous dichlorethane, were added dropwise at 5 °C. The mixture was mixed for 1 hour and then 5.53 g (0.0143 mol) of cholesterol and 1.13 g (0.0143 mol) of pyridine, dissolved in 120 ml of anhydrous dichlorethane, were added dropwise at 5 °C. First, the suspension was mixed for 1 h while the temperature was raised gradually up to the room temperature and then 6 h at 20 °C. The precipitate of pyridinium chloride was filtered out. The solvent was distilled out and the pellet was dried in vacuum (100–200 Pa) at 40 °C for 3 h, yielding 9.5 g (92%) of monoperoxided monocholesteryl pyromellitate with residual acid chloride groups. The pellet had a fawny wax-like appearance. Its characteristics are summarized as follows: content of active oxygen - 1.6% (calc. 2.1%); content of active chlorine–7.8% (calc. 9.7%); AN = 290 mg KOH/g (calc. 307 mg KOH/g); Infrared spectra were obtained using "Specord-80" apparatus within the range of 3500-500 cm^{-1}. The samples were prepared as a film obtained from CH_2Cl_2 solution and applied over KBr prism.

2.3. Modification of glass surfaces with PChP

The procedure of modification is sketched in Scheme 2. Glass plates (20 × 20 mm) were dipped into 0.2% (w/w) methanolic solution of APTES for 24 h (1). After the incubation, loosely-attached silane molecules were removed with methanol in Soxhlet's apparatus. Then the plates functionalized with APTES were dipped into 2% solution of peroxide in arid dioxan for different time (2). Similarly, loosely-attached peroxide was removed with dioxan. As a result, peroxides grafted to aminated surfaces were obtained (3).

2.4. ^{1}H NMR spectroscopy

^{1}H NMR spectra of monoperoxided monocholesteryl pyromellitate with residual acid chloride groups in DMSO-D6 solution was registered on a spectrometer, Varian VXR" spectrometer (300 MHz), internal reference tetramethylsilane.

2.5. Ellipsometry

Measurements were carried out with a commercially produced null-ellipsometer LEF-3 M, equipped with the "polarizer–compensator-specimen-analyzer" arrangement, enabling angular positions of polarization elements to be determined within a 0.01° precision. A He–Ne single-mode laser (light wavelength λ = 632.8 nm) was used as a light source. Polarization parameters of light reflected from a sample (angles Δ and Ψ) were determined using the two-zone technique (in the third and fourth measuring zone) for angle of incidence φ varied between 58° and 63° (with a 1° step). This φ -range, corresponding to the region of the pseudo-Brewster angle (where $\Delta \approx \pi/2$ or $3\pi/2$), ensures maximal sensitivity. The iterative procedure using mono- and two-layer models were used to fit the (π, Δ) data recorded at optimal experimental conditions [19] and yield average thickness d (and refractive index n) for monoperoxided monocholesteryl pyromellitate coatings. Optical parameters were determined as the average of three measurements at different spots.

2.6. Water contact angle measurements

Static contact angle experiments were performed by means of the sessile drop technique using a Lab-made apparatus. The measurements were performed at temperature 20 °C using bidistilled